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CONTENTS OF VOLUME 2, 1927.

No. 1. JANUARY.

Jitsusaburo SAMESHIMA: The Sorption of Gas by Charcoal as a Dissolution Phenomenon 1
Taku UEMURA, Naomichi YOKOJIMA and Tamimatsu ENDO: Spectrochemical Studies of Hydroxyazo-compounds. Part II 10
Kashichi ONO et Zensuke TAKEDA: Action Catalytique de la Terre Acide Japonaise sur le l-Linalol (Recherches sur l'Essence de Camphre VII) 16
Shintaro OGAWA: The Application of the Perkin Reaction to Phenolic Aldehyde 20
Yoshiyuki URUSHIBARA: On the So-called Diethyl Dicyanoglutaconate and Some of Its Derivatives 29

No. 2. FEBRUARY.

Toshiaki SHIRAI: On the Density of the Water Vapour 37
Susumu MIYAMOTO: The Effect of Alkali on the Oxidation of Ferrous Hydroxide with Air 40
Shinnosuke MATSUURA: Über das Gleichgewicht des Systems Glukose-Kochsalz-Wasser 44
Taku UEMURA, Naomichi YOKOJIMA and Tamimatsu ENDO: Spectrochemical Studies of Hydroxyazo-compounds. Part III 48
Kenji IWAMOTO: The Condensation of Phenolic Aldehydes and Their Ethers with Methyl Ethyl Ketone 51
Shigeru KOMATSU and Yasuo SASAOKA: The Occurrence of Free Pentose in Bamboo Shoots. (Studies on Japanese Plants. VIII) . 57

No. 3. MARCH.

Eiichi IWASE: Electrical Conductivities of the Salt Solutions Containing Agar 61
Teru ARIGA: The Photochemical Reactions of Colouring Matters. I. The Reversible Photochemical Reaction of Malachite Green 65
Susumu MIYAMOTO: The Effect of Alkali on the Oxidation of Sodium Sulphite with Air 74
Yojiro TSUZUKI: The Formation of Oxy-derivatives of Diphenylene Oxide from Resorcin 79

356910

No. 4. APRIL.

Manjiro SHIRADO: Über Dampfdruckmessungen Wässriger Blausäure bei 18°C. 85
Toshizo TITANI: The Viscosity of Liquids above their Boiling Points. Part I 95
Taichi HARADA: Some New Metallo-organic Oxonium Salts 105
Itizo KASIWAGI: Etudes de Dérivés du Furfural. IV. Des Dérivés Nitrés de la Série du Furyléthylène 110

No. 5. MAY.

Kunizô HUKUDA: A Simple Procedure of Semi-quantitative Spectral Analysis of Calcium, Strontium, Barium and Lithium 115
Manjiro SHIRADO: Das Spezifische Gewicht Wässriger Blausäure . . 122
Kwantaro ENDO: The Activity of Phenol in Aqueous Salt Solutions . 124
Hikozô ENDO: The Densities of Magnesium at its Melting Point . . 131
Saburo ISHIMARU: On the Preservation of the Standard Solution of Oxalic Acid and on the Reading of the Burette 134
Naoyasu SATA: Über die Dichte von System des Nikotin-Wassers . . 139
Yoshiyuki URUSHIBARA: On W. A. Noyes' Method of Preparing Ethyl Cyanacetate 143

No. 6. JUNE.

Kwantaro ENDO: The Formation of a Complex Ion in the Aqueous Solution of Silver Nitrate and Phenol 147
Susumu MIYAMOTO: The Effect of Caustic Alkali on the Oxidation of Stannous Chloride with Air 155
Toshizo TITANI: The Viscosity of Liquids above their Boiling Points. Part II 161
Shizuo HATTORI: Synthese von 3′,4′-Methylendioxyflavon, 3′,4′-Methylendioxyflavonol, 3′,4′-Dimethoxyflavon und 3′,4′-Dimethoxyflavonol 171
Takashi EGUCHI: On the Basic Nitrogen Compounds from Fushun Shale Tar, I 176

No. 7. JULY.

Eiichi IWASE: Synthesis of Red Dispersoidal Solution of Gold by means of Aqueous Extracts from Fresh Leaves of Plants. 187

Susumu MIYAMOTO: On the Oxidation of the Mixture of Stannous Chloride and Sodium Sulphite in Alkaline Solution with Air . . . 191
Toshizo TITANI: The Viscosity of Liquids above their Boiling Points. Part III 196
Itizo KASIWAGI: Action du Nitrométhane et de ses Homologues sur le Benzile. 202
Kashichi ONO and **Shuei MIYAZAKI**: On the Catalytic Action of Japanese Acid Clay upon Cineol. (Studies on Camphor Oils VIII) . 207
Bennosuke KUBOTA and **Takeo YAMANE**: A Method of Determining Molecular Weight of Organic Substances in Small Quantities by means of Freezing Point Depression 209

No. 8. AUGUST.

Jurô HORIUCHI: A Relation between Orthobaric Densities. Part II. . 213
Toshizo TITANI: The Viscosity of Liquids above their Boiling Points. Part IV 225
Taku UEMURA and **Shozo TABEI**: Spectrochemical Studies of Hydroxyazo-compounds. Part IV 229
Yoshiyuki URUSHIBARA: On the so-called Diethyl Dicyanoglutaconate and Some of its Derivatives. II 236

No. 9. SEPTEMBER.

Michael TARLÉ: The Surface Area and Sorption 243
Jitsusaburo SAMESHIMA: On Dr. Tarlé's Paper Entitled "The Surface Area and Sorption" 246
Taku UEMURA and **Shozo TABEI**: Spectrochemical Studies of Hydroxyazo-compounds. Part V 249

No. 10. OCTOBER.

Susumu MIYAMOTO: The Effect of Hydrochloric Acid on the Oxidation of Stannous Chloride with Air 259
Satoyasu IIMORI: Formation of the Radioactive Manganiferous Deposits from Tanokami, and the Source of Manganese in the Deep-sea Manganese Nodules 270
Satoyasu IIMORI: The Green Kaolin from Tanokami. Identity of the Universal Minor Constituents of the Igneous Rock with the Chromospheric Elements of the Sun 274
Yoshiyuki URUSHIBARA: On the Nitrile-esters of the Dicarboxyglutaconic Acid 278

No. 11. NOVEMBER.

Bunnosuke YAMAGUTI: The Catalysis of Nickel on the Thermal Decomposition of Methane 289
Fusao ISHIKAWA: On the Fictitious Heat of Solution of Thallous Sulphate 294
Bun-ichi TAMAMUSHI: Bemerkungen über die Zustandsgleichungen der adsorbierten Phase 299
Michael TARLÉ: A Note on Sorption 304
Yoshiyuki URUSHIBARA: Condensation of Ethyl Acetoacetate with Sodio-malonitrile. A View on the Explanation of Similar Reactions. 305
Yoshihito SAKURADA: On Carbolthionic Acids and their Esters. Part IV. A New Method of Formation for Thiamides and Thiohydrazides . 307
Itizo KASIWAGI: Etudes de Dérivés du Furfural. V. Action des Composés Organomagnésiens sur les Cétones Furyliques et Constitution de la Furylidène-méthyléthylcétone 310

No. 12. DECEMBER.

Mataichi YASUDA: The Estimation of Gold and Silver in Sea Waters 321
Yuji SHIBATA and **Tei-ichi ASAHINA**: Spectroscopical Study of Amino-acid Anhydrides. II. Light Absorptions of Some Amino-acids, Their Esters, Peptides and Anhydrides 324

Corrections to Volume 2 335
Author Index to Volume 2 337
Subject Index to Volume 2 340

THE SORPTION OF GAS BY CHARCOAL AS A DISSOLUTION PHENOMENON.

By Jitsusaburo SAMESHIMA.

Received December 13, 1926. Published January 28, 1927.

It is generally considered that the sorption of gas by charcoal is caused by the condensation of gas on the surface of the charcoal. Since Saussure's extensive research on this subject[1] nobody raise a doubt on the hypothesis of adsorption.[2] Recently, many suppositions have been proposed for the mechanism of sorption. Of them monomolecular film hypothesis of Langmuir[3] and polymolecular film hypothesis of Polanyi[4] are preeminent. None of them, however, do not sufficiently coinside with the results of experiments. McBain and others[5] have the opinion that one part of the gas absorbed is kept on the surface of the carbon and the other part diffuse into the mass of it.

I have studied the sorption of gas by charcoal for last several years[6] and recently was convinced that this phenomenon is caused by the dissolution of gas into the mass of charcoal. Of course the minimal quantity of gas may be adsorbed, positively or negatively, on the surface of the charcoal as is required by the Gibbs-Thomson's equation, but almost all quantity of gas absorbed is kept in the mass of charcoal as a solid solution. This has been proved by the facts described in this paper and by those which will be described in the later papers.

I have found no paper except Homfray's one[7] which deals the sorption of gas by charcoal as a dissolution phenomenon. There is no follower of Miss Homfray since the publication of her paper sixteen years ago, and only the adsorption hypothesis prevails throughout the scientific world.

Velocity of Sorption of Carbon Dioxide by Charcoal under Constant Pressure. The velocity of sorption of gas by charcoal was already

(1) Saussure, *Gilb. Ann.*, 70 (1814), 113.

(2) The term "adsorption" was firstly used by Kayser, *Wied. Ann.*, 14 (1881), 450. For earlier literatures see, Mülfarth, *Ann. Physik*, [4], 3 (1900), 328.

(3) Langmuir, *J. Am. Chem. Soc.*, 40 (1918), 1361.

(4) Polanyi, *Ber. deut. physik. Ges.*, 16 (1914), 1012; *Z. Elektrochem.*, 18 (1916), 55 & 26 (1920), 370.

(5) McBain, *Phil. Mag.*, 18 (1909), 916; *Z. physik. Chem.*, 68 (1909), 471; *Nature*, 117 (1926), 550. Gouy, *J. d. Phys.*, [4], 9 (1910), 457. Firth, *Z. physik. Chem.*, 86 (1914), 294. Sheldon, *Phys. Rev.*, 19 (1922), 253.

(6) Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University*, 12 (1924), 289.

(7) Homfray, *Z. physik. Chem.*, 74 (1910), 129. See Coolidge, *J. Am. Chem. Soc.*, 48 (1926), 1795.

measured by numerous authors,[1] but their experiments were not suited for the present purpose. I have measured the velocity of sorption of carbon dioxide by the cane sugar charcoal.

The charcoal was made by heating the pure saccharose from Merck in a porcellain crucible to red heat and then transfered into a quartz tube and again heated in vacuo to 1,000° for 30 minutes. The carbon dioxide was made by the action of the hydrochloric acid on the marble and passed through the sodium bicarbonate solution, concentrated sulphuric acid and phosphorus pentoxide successively. The gas was, then, frozen by liquid air, exhausted, and finally sublimed in vacuo.

The weight of charcoal was determined in the following manner. The sample is introduced into a small tube, which is then connected to an evacuating system. Heat to 300° and evacuate to a pressure less than 0.001 mm., and then hermetically sealed and weighed. The tube is then cut open and the charcoal is transfered into the measuring apparatus (A in Fig. 1). The emptied glass tube and the pieses of glass are weighed and subtracted from the former value. Of course the correction for the bouyancy of the air must be applied.

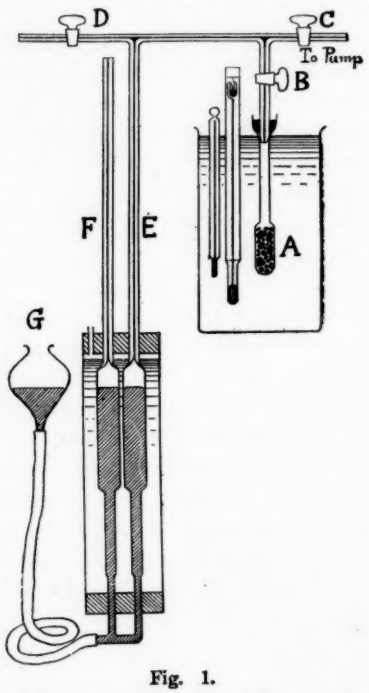

Fig. 1.

The measuring apparatus is shown in Fig. 1. A is a vessel containing the known quantity of charcoal. This is heated to 300° by an electric furnace and evacuated by using a mercury diffusion pump for 30 minutes after the pressure diminishes less than 0.001 mm. The stopcock B and C are then closed, and the carbon dioxide gas is introduced through the cock D into the graduated burette E. The burette E consists of three parts, the upper part is made of a capillary tube of 2.3 mm. diameter, and the middle part an ordinary gas burette, and the lower part a ten c.c. burette of 7 mm. diameter.

(1) Giesen, *Ann. Physik*, **10** (1903), 838. Bergter, *Ann. Physik*, **37** (1912), 472. Harned, *J. Am. Chem. Soc.*, **42** (1920), 372. Driver and Firth, *J. Chem. Soc.*, **121** (1922), 2409. Gustaver, *Kolloidchem. Beihefte*, **15** (1922), 185. Iliin, *Z. physik. Chem.*, **107** (1923), 145. Rowe, *Phil. Mag.*, [7], **1** (1926), 659.

The latter two parts are kept in a water mantle as shown in the figure to prevent the change of temperature of the gas. A thermostat is brought to A by which it is kept to 25.00°, the constancy of temperature is indicated by a Beckmann thermometer. Now the cock B is opened and the carbon dioxide gas enters into the vessel A and is absorbed by the charcoal. The mercury reservoir G is raised to keep the gas pressure as constant as possible. The pressure of gas is read by the open manometer F and a barometer. The manometer F is made of three glass tubes of the same diameters to E as shown in the figure. The whole apparatus was calibrated with mercury before being assembled. This enabled the volume of gas in the different sections of the apparatus to be reduced separately to 0°C. from their observed temperatures.

The volume of the charcoal itself has been calculated assuming the density of charcoal to be 2.10[1]. Some investigators[2] gave lower values for the density of charcoal, but the above given value is considered to be most reasonable from the fact that the charcoal has essentially identical nature to graphite.[3] The results are shown in Table 1. After the first series of observations had finished, the tube A was heated to 300° and evacuated for 30 minutes and then the second series of observations has been undertaken. Quite reproducible results were obtained as shown in the table.

TABLE 1.

Quantity of charcoal used in the experiments=0.8604 gr.

	Time. Min.	Time. Sec.	Volume of CO_2 absorbed by 1 gr. of charcoal at 25.00° (N.T.P.), in c.c.	Pressure of gas in mm. Hg.
First series.		26	36.88	763.3
		59	43.48	763.3
	2	40	47.67	763.3
	3	10	48.11	763.3
	4	45	48.99	763.3
	95		52.58	762.3
	180		52.98	761.3
	1630		53.87	760.2
	3120		53.90	755.5

(1) Howard and Hulett, *J. Phys. Chem.* **28** (1924), 1082.

(2) Cude and Hulett, *J. Am. Chem. Soc.*, **42** (1920), 391. Harkins and Ewing, *J. Am. Chem. Soc.*, **43** (1921), 1787.

(3) Debye and Scherrer, *Physik. Z.*, **18** (1917), 300. Asahara, *Japanese Journal of Chemistry*, **1** (1922), 35.

TABLE 1. (*Continued.*)

	Time. Min.	Sec.	Volume of CO_2 absorbed by 1 gr. of charcoal at 25.00° (N. T. P.), in c.c.	Pressure of gas in mm. Hg.
Second series.		33	39.32	760.0
	2	50	47.86	760.0
	10	27	50.26	760.0
	12	25	50.44	760.0
	13	45	50.57	760.0
	15	20	50.75	760.0
	22	12	51.18	760.0
	25	55	51.36	760.0
	35	0	51.65	760.0
	40	30	51.77	760.0
	49	30	51.95	760.0
	65		52.24	760.0
	91		52.52	760.0
	146		52.85	760.0
	199		53.06	760.0
	220		53.11	760.0
	257		53.16	760.0
	281		53.22	760.0
	353		53.32	760.0
	387		53.37	760.0
Third series.		15	34.38	768.2
		25	37.91	768.2
		44	42.22	768.2
		61	44.37	768.2
	4	25	48.81	760.0
	26	10	51.25	757.7
	32	20	51.59	760.0
	35		51.71	760.0
	40		51.78	760.0
	42		51.89	760.0
	55		52.13	760.0
	79		52.42	760.0
	196		53.12	760.0
	294		53.23	760.0
	315		53.28	760.0
	365		53.33	760.0
	1470		53.95	761.4
	1610		53.95	760.0
	3080		54.04	760.0
	3205		54.03	760.0

After the sorption had been measured, the charcoal was powdered in an agate mortar as fine as possible. The powdered charcoal was put into a glass tube and was connected to an evacuating system, heat to 300° and evacuated for 30 minutes, then hermetically sealed and weighed, in the same manner as in the case of granular charcoal. The powder was transfered into the vessel A in Fig. 1 and then measured the quantity of absorption of carbon dioxide gas. The results are shown in Table 2.

TABLE 2.

Quantity of powder charcoal used in the experiments = 0.8752 gr.

Time. Min.	Time. Sec.	Volume of CO_2 absorbed by 1 gr. of powder charcoal at 25.00° (N.T.P.) in c.c.	Pressure of gas in mm. Hg.
	22	44.54	760.0
	33	46.63	760.0
	43	47.68	760.0
	57	48.73	760.0
2	48	51.01	760.0
3	54	51.38	760.0
5	8	51.74	760.0
7	0	52.09	760.0
10	50	52.43	760.0
18	20	52.72	759.7
29	30	52.94	760.0
41		53.11	760.0
100		53.33	760.0
140		53.44	760.0
235		53.52	760.0
295		53.55	760.0
1440		53.85	760.0
1785		53.91	760.0
2880		54.01	760.0
2910		54.00	760.0
2975		53.97	760.0
3110		53.97	760.0

Graphically it becomes as Fig. 2. In this figure the logarithm of the time in seconds is taken in abscissa and the absorbed volume of carbon dioxide in ordinate.

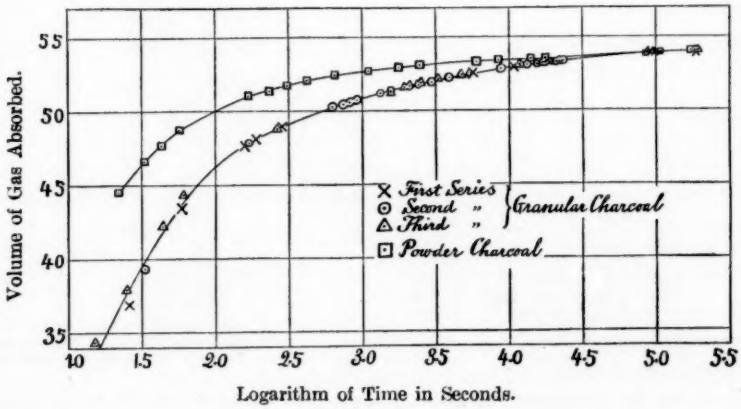

Fig. 2.

We see, from the above results, that the absorbed quantity of carbon dioxide by granular charcoal and by powder charcoal are quite the same. Moreover, the powder charcoal absorbs the gas more rapidly than the granular one. If we assume that the gas dissolves into the charcoal, then the above phenomena can be explained very smoothly. The dissolved quantity of gas depends only upon the amount of charcoal, and does not depend upon the surface area of it. So the same amount of charcoal absorbs the same quantity of gas, so long as the purity and the chemical nature of the carbon are the same, no matter what the surface area may be. By powdering the charcoal, the surface area must increases, so the velocity of dissolution must, of course, increases. From the adsorption hypothesis, the adsorbed quantity of gas must increases or decreases[1] by powdering the substance, but in my experiment it is not so. Quantitative discussions may appear in a later paper.

The Amounts of Carbon Dioxide Absorbed by Various Kinds of Charcoals.[2] The absorptive capacities were measured of carbon dioxide by the various kinds of charcoals and the results are shown in Table 3. In each case the capacities were measured after the charcoals had been heated to 300° in vacuo.

TABLE 3.

Material from which the charcoal was obtained	Treatment.	Temp. °C.	Press. mm.	Volume of CO_2 absorbed by 1 gr. of charcoal (N.T.P.) c.c.	Ash content %
Bamboo wood.	The material was carbonized at 400°–500°, and then heated to 800° for 1 hour.	20.1	759	44.8	3.0
Cherry wood.	do.	22.0	758	43.0	1.5
Ebony wood.	do.	25.0	758	36.7	14.0
Cork.	do.	24.0	756	49.0	7.2
Cocoanut shell.	do.	23.2	754	46.3	2.8
Rice.	do.	25.0	755	46.0	1.7
Soy-bean.	do.	16.2	765	3.6	20.5
Kahlbaum's "Kohle activ".	—	23.3	758	44.2	6.1
Bamboo wood.	The charcoal was boiled with aqua regia, washed with water and heated to 300°	25.0	758	43.4	0.8

(1) See Freundlich, "Kapillarchemie" 3rd. ed. (1923), p. 177.

(2) More detailed descriptions are found in the *Journal of the Chemical Society of Japan* (in Japanese), **47** (1926), 715.

TABLE 3. (*Continued.*)

Material from which the charcoal was obtained	Treatment	Temp. °C.	Press. mm.	Volume of CO_2 absorbed by 1 gr. of charcoal (N.T.P.) c.c.	Ash content. %
Cane sugar.	The sugar was carbonized in a crucible and then heated to 1,000° in vacuo for 30 minutes.	25.0	760	54.0	0
Carbon* monoxide soot.	CO was decomposed by hot iron. The charcoal was treated with HCl.	25.5	759	7.1	5.9 (Fe_2O_3)
Naphthalene** soot	———	25.0	762	38.0	—
Anthracite.	Anthracite was treated with HNO_3 and heated to 1,000°	20.2	765	45.6	8.1

* By the courtesy of Dr. Asahara in the Institute of Physical and Chemical Research.
** Made in the Laboratory of Prof. Michaelis in Aichi Medical University, Nagoya.

We see from Table 3 that the amount of absorbed carbon dioxide at ordinary temperatures (20–25°) by various kinds of charcoals are nearly equal in each other, viz. 35–50 c.c., notwithstanding the materials from which the charcoals have been made are so divergent. In the case of the soy-bean charcoal, the ash content is so high as 20% and such an impure charcoal cannot be compared with other purer charcoals. The bamboo charcoal was made by the carbonization of the hard fibrous stem of that tree, the sugar charcoal was made by the carbonization of the fused mass of sugar, while naphthalene soot by the imcomplete oxidation of the combustible vapour. It is not conceivable that so different materials give the charcoals of nearly same surface area. The surface area must, of course, be different in each charcoals, while they show nearly equal absorptive capacities. This fact can only be explained by the dissolution theory and not by the adsorption theory. The content of ash and other impurities will change the absorptive capacities of the charcoals, just as the dissolved salts or alcohol diminishes the solubility of hydrochloric acid gas in the water. The "activation" process is probably a process of removing the impurities and enlarging the surface area by etching which will enable the ability of rapid absorption of the gas.

One gram of the pure cane sugar charcoal absorbs 54.0 c.c. of carbon dioxide (N.T.P.) at 25.0° and under the gas pressure of 760 mm. We may take this quantity as the solubility of carbon dioxide in pure charcoal. For impure charcoal the solubility of gas will change according to the amounts, the chemical nature and the state of existence (i.e. physical mixture, solid solution or compound) of the impurities. The soy-bean charcoal and the

carbon monoxide soot are the examples of the great effect of impurities. The carbon dioxide is an unsuitable gas to test the effect of impurities, because CaO, MgO etc. in the ash will chemically absorb this gas. The experiments for other gases will be undertaken later.

Absorptions of Carbon Dioxide by Charcoal at Various Temperatures and Pressures.[1] The determinations were made of the absorption amounts of carbon dioxide by another sample of bamboo charcoal at different temperatures and pressures and the results are summarized in Table 4.

Table 4.

Volumes of CO_2 absorbed by 1 gr. of bamboo charcoal (N.T.P.) in c.c.

Press. \ Temp.	0°	10°	20°	30°	40°
50 mm.	15.5	11.7	9.0	6.3	3.6
100 mm.	22.1	17.4	13.7	10.1	6.3
200 mm.	30.0	24.8	20.1	15.4	10.6
300 mm.	35.0	29.4	24.5	19.2	14.2
400 mm.	38.8	32.8	27.9	22.3	17.1
500 mm.	41.6	35.6	30.8	25.0	19.4
600 mm.	43.9	38.1	33.1	27.1	—

If we plot the logarithm of the volume against the logarithm of the pressure, Fig. 3 is obtained. Form Fig. 3 we see that the Freundlich's formula can hardly be applied in this case.

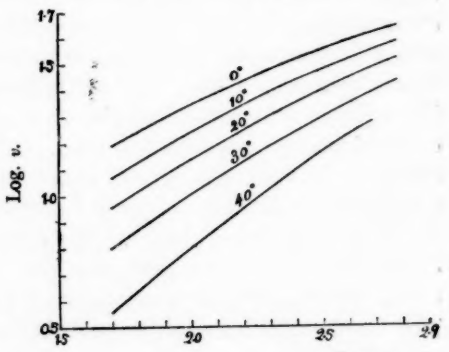

Fig. 3.

Numerous authors have tested whether the Henry's law can be applied for the absorption of gases by solids. In the case of hydrogen the law is applicable,[2] but in other gases it is not so. In Fig. 3 we see that the tangent of curves approach to unity at the high temperature and low pressure, for example at 40° it becomes,

$$\frac{d(\log v)}{d(\log p)} = \frac{4}{5}, \qquad \text{or} \qquad v = kp^{0.8}$$

(1) This experiment was done in 1922 in the Chemical Laboratory of the Tohoku Imperial University, Sendai.

(2) Titoff, *Z. physik. Chem.*, **74** (1910), 641.

where v denotes the absorbed volume of gas, p the pressure and k a constant. The charcoal absorbs too much carbon dioxide to be applied the Henry's law, just as the cases of the dissolutions of ammonia or hydrochloric acid gas in the water. The amount of absorbed gas increases by lowering the temperature, which is quite similar to the dissolution of gas in water. There are parallelisms between the temperature effect on the absorption of gas by charcoal and by water.

Change of Absorption Amount by the Change of Modification. It is generally known that a substance in amorphous modification absorbs much gas than its crystalline modification.(1) It is doubtful that there is really amorphous substance in solid modification from the standpoint of the phase rule, X-ray analysis or colloid chemistry. Some of them may be the supercooled liquids and others may be the imperfect crystals of somewhat irregular atomic arrangements. But in any case, the so-called amorphous substance is the modification which will be situated between the perfect crystalline phase and the liquid phase. So it is expected that the solubility of gas by the amorphous modification is greater than that by the crystalline one, and probably less than that by the liquid if a comparison at the same temperature could be done. The absorptions of gases by silica gel, alumina or some of the fine powder of metals may ascribe to this cause.

The author wishes to express his thanks to Dr. G. Asahara and Dr. T. Totsuka for furnishing some of the charcoals. The author's thanks are also due to Mr. M. Kishino and Mr. T. Watanabe for their assistances in the experiments.

Summary.

1. The velocities of absorptions of carbon dioxide by the granular and the powder charcoals have been measured.

2. The velocity of absorption by the granular charcoal is smaller than that by the powder one.

3. It was confirmed that the absorption amounts by the granular and by the powder charcoal are the same.

4. The solubility of carbon dioxide in one gram of pure cane sugar charcoal at 25.0° and under 760 mm. has been determined to be 54.0 c.c. (N.T.P.).

5. The amounts of absorptions of carbon dioxide by various kinds of charcoals have been measured. Most of them absorb nearly equal amount of the gas, notwithstanding the divergence of the materials from which the charcoals were made.

6. The amounts of absorptions of carbon dioxide by bamboo charcoal at various temperatures and pressures have been measured.

(1) See Freundlich "Kapillarchemie" 3rd. ed. (1923), p. 178.

7. The fact that the amorphous substance absorbs more gas than the crystalline one has been interpreted.

8. All of the facts mentioned above favoured the dissolution theory for the sorption of gas by charcoal.

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SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART II.[1]

By **Taku UEMURA, Naomichi YOKOJIMA** and **Tamimatsu ENDO.**

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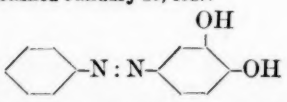
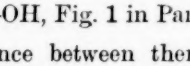
1. Benzeneazocatechol[2] **(Benzeneazopyrocatechin),**



Although the addition of KOH to this substance induces a change of colour in the solution from yellow to orange, only a slightly bathochromic influence can be observed from the absorption curve (Fig. 1). When we compare Fig. 1 with the absorption curve of No. 1 compound ( , Fig. 1 in Part I of this paper), we can ascertain a considerable difference between them. We think this is due to the hydroxyl-group of the meta-position with respect to the azo-group. Then,

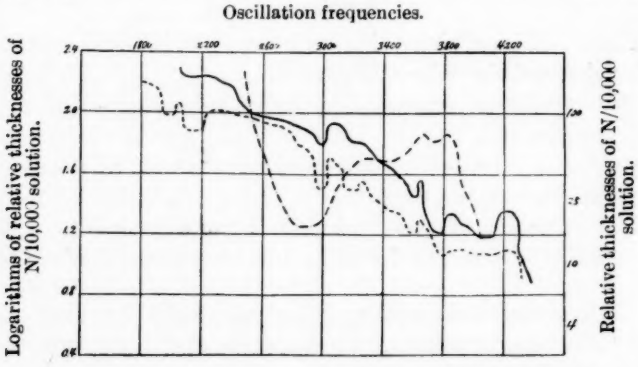


Fig. 1.

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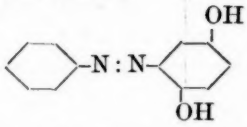
(1) Part I of this paper has been published in this journal 1 (1926), 260. N.B. In this paper, in the 12th line from the bottom on page 261, the phrase "the bathochromic and hyperchromic influences are easily observed" should be changed to "the bathochromic influence is easily observed".

(2) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1440.

A-form is naturally assigned to the neutral solution, but the orange alkaline solution is perhaps the mixture of A-form and R-form.

2. Benzeneazoquinol[1] (Benzeneazohydroquinone),



This substance is hardly affected in colour by the addition of KOH, and its absorption curves (Fig. 2) are also represented as can be expected. Only A-form exists in the solution of this compound.

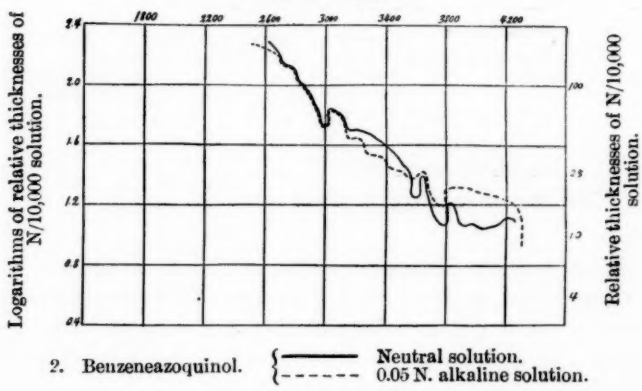
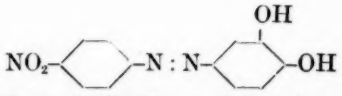
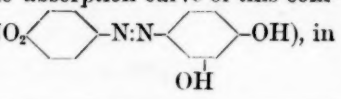


Fig. 2.

3. p-Nitrobenzeneazocatechol[2] (p-Nitrobenzeneazopyrocatechin),

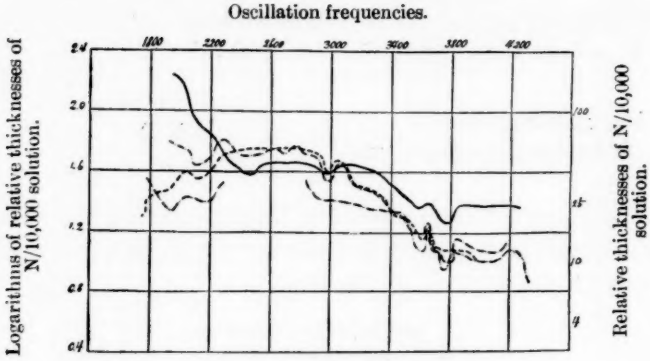


Bathochromic and hyperchromic effects through alkali are observed in the solution of this compound. As the range of the red coloured solution is quite short, it changes into blue very quickly. N/1,000 alkaline solution is already blue, but this blue solution loses its shade, changes into reddish brown after standing one day, and can no more regain its former shade. We may give A-form to the neutral solution and B-form to the blue alkaline solution. According to the meta hydroxyl with respect to the azo-group, a great difference can be observed between the absorption curve of this compound (Fig. 3) and that of No. 5 compound (

), in Part I of this paper.

(1) Beilstein, "Handbuch der Crganischen Chemie", IV (1899), 1447.

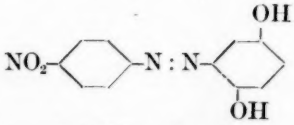
(2) Ibid., IV (1899), 1440.


Oscillation frequencies.
Logarithms of relative thicknesses of N/10,000 solution.
Relative thicknesses of N/10,000 solution.

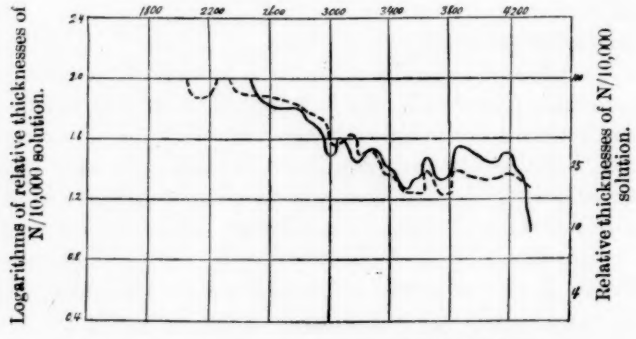
3. p-Nitrobenzeneazocatechol. ——— Neutral solution. - - - - - 0.048 N. alkaline solution. —·—·— „ „ (after 3 days.) —··—··— „ „ (after 4 days.)

Fig. 3.

4. p-Nitrobenzeneazoquinol[1] (p-Nitrobenzeneazohydroquinone),



We notice a slight change in colour through KOH, that is, by the addition of an alkali, a yellowish red neutral solution becomes orange, but this orange returns to yellow after one day and deos not take the former shade again. Then A-form can be assigned to the neutral solution, and probably R-form to the orange state (Fig. 4.).

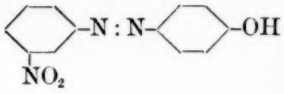

Oscillation frequencies.
Logarithms of relative thicknesses of N/10,000 solution.
Relative thicknesses of N/10,000 solution.

4. p-Nitrobenzeneazoquinol. ——— Neutral solution. - - - - - 0.05 N. alkaline solution.

Fig. 4.

(1) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1447.

5. m-Nitrobenzeneazophenol,[1]



The yellow neutral solution changes into red when an alkaline solution is added. The bathochromic influence due to KOH can clearly be seen in the absorption curve (Fig. 5). We can certainly give A-form to the neutral solution and R-form to the alkaline solution which cannot have B-form owing to the meta nitro-radical with respect to the azo-group.

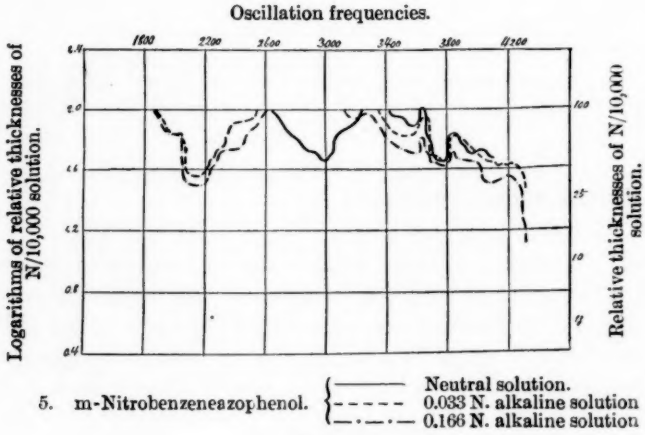
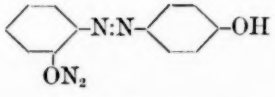


Fig. 5.

6. o-Nitrobenzeneazophenol[1]



The very same colour changes in No. 5 compound can be easily observed in this case, that is, we recognise bathochromic and hyperchromic effects when the solution is alkaline, but can never get the blue solution. Therefore, A- and R-forms only exist in o-Nitrobenzeneazophenol solution (Fig. 6).

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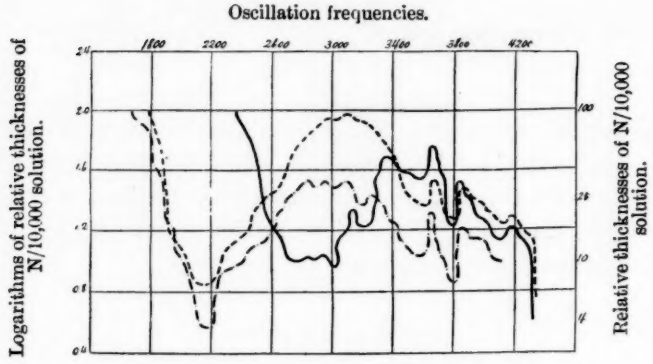
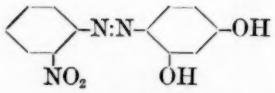
(1) Beilstein, "Handbuch der Organischen Chemie", IV (1899), 1410.



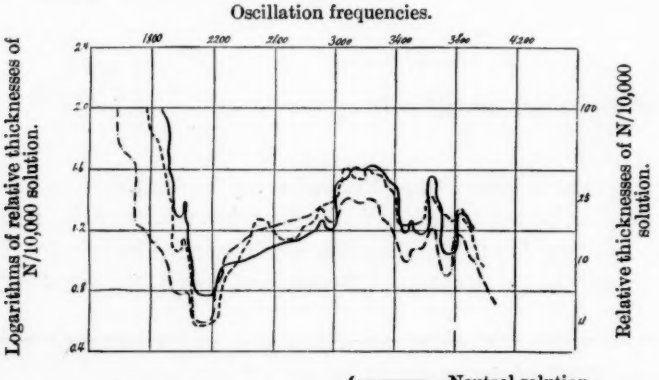
6. o-Nitrobenzeneazophenol. { Neutral solution. / 0.05 N. alkaline solution. / 1.44 N. alkaline solution.

Fig. 6.

7. o-Nitrobenzeneazoresorcinol,[1]



Only the red alkaline solution of this compound can be easily obtained, and A- and R-forms can be respectively given to the neutral and alkaline solutions (Fig. 7). It is, therefore, proved that the nitro-radical which is in the ortho-position with respect to azo-group cannot take the isonitro-structure (See No. 6 compound).

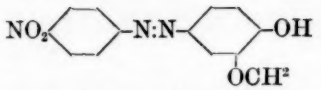


7. o-Nitrobenzeneazoresorcinol. { Neutral solution. / 0.0567 N. alkaline solution. / 1.12 N. alkaline solution.

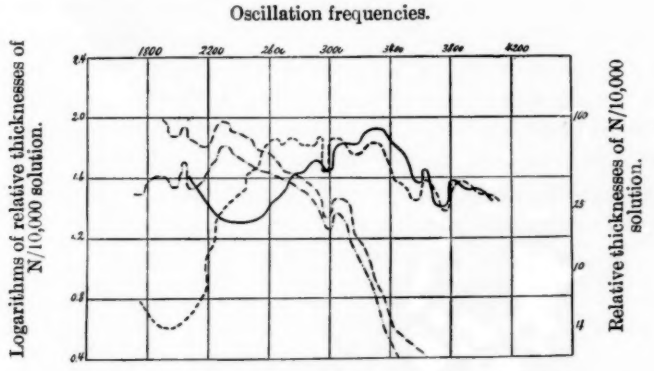
Fig. 7.

(1) Obtained from o-nitraniline and resorcinol.

8. p-Nitrobenzeneazoguaiacol,[1]



The yellow neutral solution changes into red by the addition of alkali like many other hydroxyazo-compounds. In this case, fairly remarkable bathochromic and hyperchromic influences through alkali can be found, and of course, A- and R-forms can be respectively assigned to the two different coloured solutions. (Fig. 8).

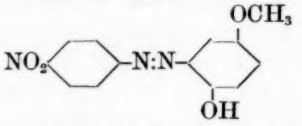


8. p-Nitrobenzeneazoguaiacol. ——— Neutral solution. - - - - - 0.8 N. alkaline solution.

9. p-Nitronenzeneazohydroquinone mono-methyl ether. —·—·— Neutral solution. —··—··— 0.045 N. alkaline solution.

Fig. 8.

9. p-Nitrobenzeneazohydroquinone mono-methyl ether,[2]



The yellowish red neutral solution changes first into purple by the addition of alkali, and then, after one hour turns brownish yellow. Slight bathochromic and hyperchromic effects due to alkali can be observed in that case (Fig. 8). From the absorption curve, we will give A-form to the neutral solution and R-form, not B-form, to the alkaline solution.

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(1) Obtained from p-nitraniline and guaiacol.

(2) Obtained from p-nitraniline and hydroquinone mono-methyl ether, which is synthetized with hydroquinone, sodium-methylalcoholate and methyliodide.

ACTION CATALYTIQUE DE LA TERRE ACIDE JAPONAISE SUR LE L-LINALOL. (RECHERCHES SUR L'ESSENCE DE CAMPHRE VII)

Par **Kashichi ONO** et **Zensuke TAKEDA.**

Reçu le 8 décembre 1926. Publié le 28 janvier 1927.

L'un de nous a indiqué dans le précédent mémoire[1] que les alcools terpéniques cycliques se transforment en hydrocarbures correspondants par déshydratation catalytique de la terre acide Japonaise. On sait déjà que le linalol se transforme sous l'action du chlorure de zinc ou du bisulfate de potassium en dipentène et terpinène[2] ou l'anhydrogéraniol.[3] Le but de notre étude est de rechercher, si les reactions entre le linalol et la terre acide Japonaise se passent d'une manière analogue

Partie expérimentale. Le prodiut employé est le " linalol pur extra " qui montre les constantes physiques suivantes,

$$d_4^{15} = 0.8731\,; \quad n_D^{19} = 1.4647\,; \quad [\alpha]_D = -14.2'$$

Soumis d'abord à la distillation fractionnée, nous avons pris pour nos essais exclusivement la fraction 197–199° pour laquelle nous avons trouvé les propriétés suivantes,

$$d_4^{22.5} = 0.8604\,; \quad n_D^{22.5} = 1.4610\,; \quad [\alpha]_D = -15.26°\,; \quad \text{R.M.} = 49.158$$

500 gr. de l-linalol et 50 gr. de la terre acide Japonaise[4] sont chauffés à 159° au bain d'huile en agitant vigoureusement comme il avait été décrit dans le précédent memoire. Après avoir chauffé pendant 85 minutes la réaction devint violente et un produit huileux commença à distiller. Le liquide distillé et le residue sont ensuite traités par la vapeur d'eau.

(I) 100 gr. ($d_4^{23} = 0.8602$; $n_D^{25} = 1.4694$) de produit ont été rectifiés sous 20–22 mm. qui donnent les fractions suivantes,

	Fraction.	Rendement.	n_D^{25}
(I)	30—70°	0.4 gr.	1.4711
(II)	70—80°	18.8	1.4715
(III)	80—8 .°	15.8	1.4721
(IV)	85—90°	4.5	1.4720
(V)	90—95°	3.2	1.4691
(VI)	95—100°	8.6	1.4649

(1) Ce journal, 1 (1926), 248.
(2) Bertram et Walbaum, *J. prakt. Chem.*, II, 45 (1892), 601.
(3) Semmler, *Ber.*, 24 (1891), 682.
(4) Pour nos essais la terre acide Japonaise a été desséchée à 100°.

(*suite*)

	Fraction.	Rendement.	n_D^{25}
(VII)	100—105°	21.2 gr.	1.4629
(VIII)	105—1 0°	7.1	1.4678
(IX)	110—115°	4.7	1.4741
(X)	115—120°	4.3	1.4781
(XI)	120—125°	2.2	1.4787
(XII)	125—130°	0.6	1.4788
(XIII)	au-dessus 130°	4.7	1.5011

Le mélange des fractions (I) à (IV) a été soumis cinq fois à la distillation fractionnée sous 21 mm. et nous pouvions en obtenir cinq fractions

A	60—65°	0.2 gr.
B	65—68°	5.4
C	68—70°	6.1
D	70—72°	6.0
E	72—74°	2.6

Après redistillation de la fraction (B), $d_4^{22.5} = 0.8175$; $n_D^{22.5} = 1.4670$; $[\alpha]_D = +3.83°$; R. M. = 46.201, en présence du sodium métallique, nous arrivions à séparer une fraction principale bouillante vers 67–68° sous 21 mm., pour laquelle nous avons trouvé les constantes physiques suivantes qui nous indiquent des données très voisines du myrcène. P. E. = 67–68° sous 21 mm. ou 169–171° sous 762 mm. ; $d_4^{19} = 0.8097$; $n_D^{19} = 1.4674$; R. M. = 46.635 ; $[\alpha]_D = \pm 0$.

Analyse : 0.1165 gr. subst. donne 0.3743 gr. CO_2 et 0.1145 gr. H_2O. (Trouvé, C = 87.61 ; H = 10.99. Calculé pour $C_{10}H_{16}$, C = 88.15 ; H = 11.85 %).

La fraction (C) bouillante vers 68–70° sous 21 mm., $d_4^{20.5} = 0.8296$; $n_D^{20} = 1.4729$; R. M. = 46.024 est probablement un mélange d'hydrocarbures terpéniques cycliques et oléfiniques.

La fraction (D) bouillante vers 70–72° sous 21 mm., $d_4^{22} = 0.8408$ $n_D^{21} = 1.4771$; R. M. = 45.755 ; $[\alpha]_D = +5.92°$, est identique au limonène. A la rectification sous pression ordinaire sur du sodium métallique on obtient un d-limonène bouillant vers 175–176° sous 765 mm., $d_4^{21} = 0.8416$; $n_D^{21} = 1.4767$; R. M. = 45.646 ; $[\alpha]_D = +6.27°$.

Analyse : 0.2008 gr. subst. donne 0.6476 gr. CO_2 et 0.2156 gr. H_2O. (Trouvé, C = 87.94 ; H = 12.00. Calculé pour . $C_{10}H_{16}$, C = 88.15 ; H = 11.85 %). Pour l'identification complète de notre limonène, nous l'avons transformé en tetrabromure fondant à 104–105°.

Nous avons constaté que la fraction (VII) contient encore une quantité notable de linalol bouillant vers 97–99 sous 21 mm., $d_4^{23} = 0.8617$; $n_D^{23} = 1.4650$; $[\alpha]_D = -10.50°$

Le mélange des fractions (IX) à (XIII) est chauffé pendant quatre heures au bainmarie à 80° avec l'anhydride phtalique en présence du benzène déshydré et on a laissé reposer une nuit. Après avoir separé l'excès d'anhydride phtalique par filtration, on a chassé le benzène dans le vide et on a extrait l'huile residuelle avec l'éther. La solution ethérée est traitée à plusieurs reprises par une solution de carbonate de soude pour éliminer l'éther phtalique acide du géraniol. On lave ensuite la solution éthérée avec de l'eau, et après l'avoir séchée sur du sulfate de sodium anhydre, on a chassé l'éther.

En distillant le residu sous 20 mm., on obtient les fractions suivantes :

		n_D^{18}
103—108°	0.1 gr.	1.4790
108—110°	2.9	1.4812
110—115°	0.9	1.4827
115—120°	1.1	1.4841
au-dessus 120°	6.4	——

La fraction bouillante vers 108–110° est identique au terpinéol $C_{10}H_{18}O$.

Analyse : 0.1302 gr. subst. donne 0.3694 gr. CO_2 et 0.1304 gr. H_2O. (Trouvé, C = 77.36 ; H = 11.19. Calculé pour $C_{10}H_{18}O$, C = 77.92 ; H = 11.78 %) $d_4^{18} = 0.9362$; $n_D^{18} = 1.4812$; R. M. = 46.873, calc. pour $C_{10}H_{18}O$. $F_1 = 47.238$; $[\alpha]_D^{18} = +14.03°$.

En traitant cette fraction par l'isocyanate de phényle, on obtient la phényluréthane de α-terpinéol, fondant à 112–113° trouvé identique au produit déjà obtenu par Wallach et Kerkhoff.[1]

La solution alcaline qui contient le géraniol, est acidulée par l'acide sulfurique dilué, et on l'extrait à l'éther. La solution éthérée est traitée par la soude et le liquide, qui contient maintenant le sel sodique est evaporé sous pression réduite. On obtient une masse cristalline brune claire qu'on saponifie par la potasse alcoolique à 10 pour 100. Après évaporation de l'alcool on y ajoute de l'eau et extrait la solution deux fois à l'éther. La solution éthérée est lavée à l'eau, séchée sur du sulfate de sodium anhydre. On chasse l'éther et le résidu huileux qui posséde l'odeur de géraniol, a donné, en distillant sous 20 mm., les fractions suivantes.

		n_D^{18}
à 122°	0.2 gr.	1.4773
122—125°	1.0	1.4776
125—128°	0.3	1.4778
au-dessus 128°	0.8	

(1) *Liebig's Ann. Chem.*, 275 (1893), 104.

Nous avons constaté que la fraction bouillante vers 122–125° sous 20 mm. est identique au géraniol avec les propriétés suivantes, $d_4^{18} = 0.8822$; $n_D^{18} = 1.4776$; R.M. = 49.424, calc. pour $C_{10} H_{18} O F_2 = 48.971$; $[\alpha]_D = \pm 0$.

Analyse : 0.1419 gr. subst. donne 0.4062 gr. CO_2 et 0.1429 gr. H_2O. (Trouvé, C = 78.06 ; H = 11.25. Calculé pour $C_{10} H_{18} O$, C = 77.92 ; H = 11.78 %).

(II) 90 gr. du résidu jaunâtre visqueux de la distillation à la vapeur d'eau ($d_4^{22} = 0.9164$; $n_D^{22.5} = 1.5061$; l'indice l'acétyle = 72.35, c'est-à-dire 21.04 % de l'alcool $C_{15} H_{26} O$), sont distillés sous 18—20 mm. et ils ont donné les fractions suivantes,

105—115°	0.2 gr.	160—185°	0.6 gr.
115—125°	0.9	185—200°	20.7
125—140°	0.9	200—210°	13.2
140—160°	1.2		

Les deux fractions (185–200° et 200–210°) sont encore distillées sous 20 mm.

135—184°	0.7 gr.	193—196°	4.8 gr.
184—187°	3.3	196—200°	7.8
187—190°	6.0	200—204°	1.7
190—193°	3.4	204—207°	1.2

La fraction bouillante vers 187–190° sous 20 mm. est identique à l'alcool sesquiterpénique oléfinique $C_{15} H_{26} O$.

Analyse : 0.1329 gr. subst. donne 0.3929 gr. CO_2 et 0.1391 gr. H_2O. (Trouvé, C = 80.62 ; H = 11.70. Calculé pour $C_{15} H_{26} O$, C = 81.01 ; H = 11.78 %). $d_4^{21.5} = 0.90197$; $n_D^{22} = 1.4942$; R. M. = 71.743, calc. pour $C_{15} H_{26} O F_3 = 71.594$.

La fraction bouillante vers 196–200° sous 20 mm. semble identique à l'oxyde diterpénique déjà obtenu par Semmler et Jonas.[1]

Analyse : 0.1301 gr. subst. donne 0.3989 gr. CO_2 et 0.1387 gr. H_2O. (Trouvé, C = 83.61 ; H = 11.92. Calculé pour $C_{20} H_{34} O$, C = 82.63 ; H = 11.81 %). $d_4^{21.5} = 0.9186$; $n_D^{21} = 1.4946$; R. M. = 92.083, calc. pour $C_{20} H_{34} O F_2 = 90.851$; $[\alpha]_D = \pm 0$.

Il résulte de l'étude entreprise que l'action de la terre acide Japonaise sur l-linalol est demontrée par une réaction des déshydratations, par une transposition intramoléculaire, par la formation d'un noyau et par une polymérisation.

Laboratoires de Saiséi-shono Kwaisha à Kobe.

(1) *Ber.*, 52 (1914), 2079.

THE APPLICATION OF THE PERKIN REACTION TO PHENOLIC ALDEHYDES.

By Shintaro OGAWA.

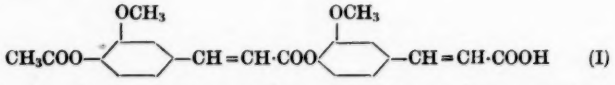
Received December 14, 1926. Published January 28, 1927.

It has been shown by Tiemann and his collaborators[1] that acetyl derivatives of hydroxycinnamic acids are formed when phenolic aldehydes, such as vanillin and p-hydroxybenzaldehyde, are heated with acetic anhydride and fused sodium acetate. However, the melting points of the acetyl derivatives obtained by this method were always not sharp. This fact was accounted for by Vorländer[2] as due to the characteristic nature of liquid crystals in the case of p-acetyloxycinnamic acid, and by Kobayashi in the case of acetylferulic acid[3], as a special peculiarity of the acid. According to my observation, I am inclined to the opinion that these substances are impure.

The author applied Perkin's reaction to vanillin and p-hydroxybenzaldehyde respectively, and subjected the products to fractional crystallisation. In the former case, the condensation product was separated into two substances and in the latter, into three.

The product obtained from vanillin consisted of a mixture of acetylferulic acid, $C_{12}H_{12}O_5$, m. p. 195–195. 5,° and substance (A) of unknown structure, $C_{22}H_{20}O_8$, m. p. 250° (decomp.), which are separated by fractional crystallisation from alcohol and glacial acetic acid, the latter being the less soluble.

The presence of one acetyl, one carboxyl and two methoxyl groups in the latter substance was proved and, on hydrolysis, it was converted into ferulic acid in an almost quantitative yield. From these facts and from its method of formation it seemed possible that the constitutional formula of this substance might be (I), although the number of double bonds was not determined.



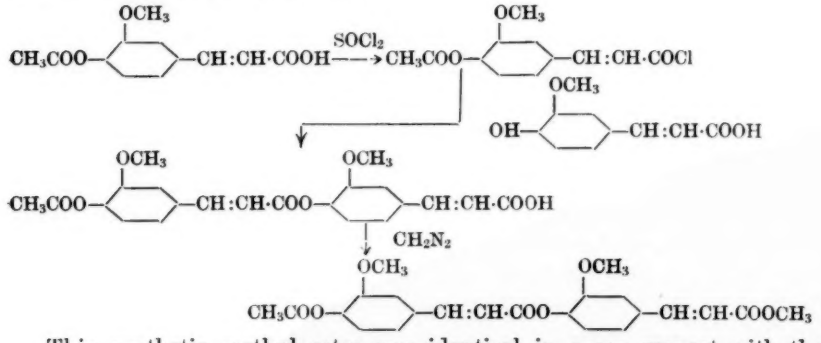
(I)

Owing to the decomposition of this acid at the melting point, it seemed desirable to prepare at first its stable derivative for indentification. The methyl ester was first synthesised by the action of diazomethane on the acid and found to be suitable for this purpose, the melting point being 204–205.5°.

The methyl ester of the substance corresponding with formula (I) was synthesised by the condensation of acetylferuloyl chloride with ferulic acid

(1) *Ber.*, **10** (1877), 65; **11** (1878), 647.
(2) *Ber.*, **39** (1906), 808.
(3) *Bulletin of the Institute of Physical and Chemical Research* (in Japanese), **4** (1925), 575.

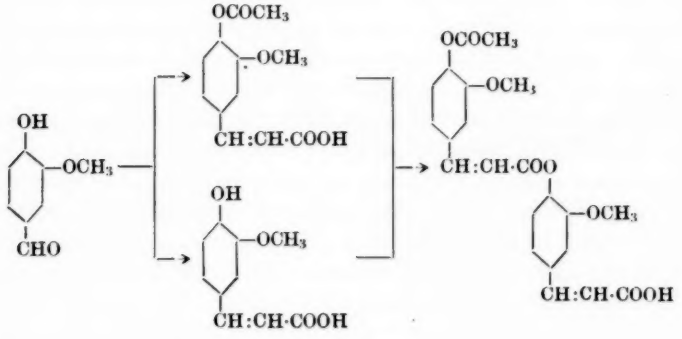
in the presence of pyridine and subsequent methylation with diazomethane, as shown in the following scheme:



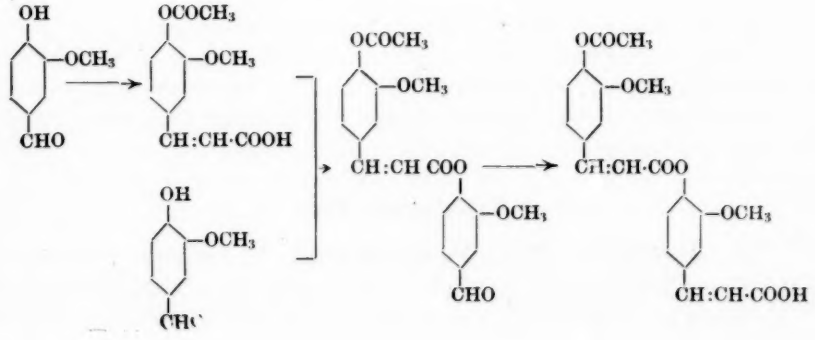
This synthetic methyl ester was identical in every respect with the methyl ester of substance (A).

The mechanism of the formation of substance (A) is accounted for by one of the following schemes, viz. (B) or (C):

(B)



(C)

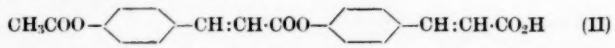


This view receives some support from the fact that the derivatives of cinnamic acid were the sole products of the action of acetic anhydride and fused sodium acetate on derivatives of vanillin which contain no phenolic hydroxyl, such as acetylvanillin and veratraldehyde.

In the case of p-hydroxybenzaldehyde, the condensation product was separated into three substance, (a) m.p. 205–205.5°; (b) m.p. 222–223° (decomp.); and (c) m.p. 231° (decomp.).

Substance (a) had the composition, $C_{11}H_{10}O_4$, and was identified as p-acetyloxycinnamic acid by analysis, molecular weight determination and by the fact that it was converted into p-hydroxycinnamic acid by hydrolysis in a good yield.

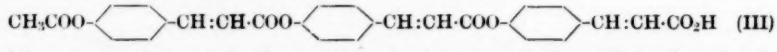
Substance (b), $C_{20}H_{16}O_6$, gave, on hydrolysis, p-hydroxycinnamic acid in an almost quantitative yield and was converted into its methyl ester, $C_{21}H_{18}O_6$, m.p. 166–167°. It is very probable judging by analogy with the case of vanillin that the constitutional formula of this substance would be 4-p-acetyloxycinnamoyl oxycinnamic acid (II),



(II)

The author synthesised the methyl ester corresponding with formula (II) in an exactly similar manner to the preparation of methyl acetylferuloylferulic acid. The synthetic methyl 4-p-acetyloxycinnamoyloxycinnamate was identical in all respects with the methyl ester of substance (b).

Substance (c) was insoluble in almost all organic solvents or camphor, and slightly soluble in hot nitrobenzene. As its molecular formula has not yet been determined, an empirical formula, $C_{29}H_{22}O_8$, only is at present assigned to it. It was converted into p-hydroxycinnamic acid by treatment with caustic soda and yielded a methyl ester having an empirical formula, $C_{30}H_{24}O_8$, when methylated with diazomethane. The author considers it to be best represented by formula (III).



(III)

The mechanism of the formation of substance (b) is explained as in the case of that of acetylferuloylferulic acid, and in the support of this view, the condensation product with anisaldehyde was only 4-methoxycinnamic acid.

The application of Perkin's reaction to the other phenolic aldehydes are now in progress.

Experimental Part.

The Application of the Perkin Reaction to Vanillin. *Isolation of Acetylferuloylferulic Acid,* $[(CH_3CO_2)(CH_3O)C_6H_3CH{:}CH{\cdot}CO_2](CH_3O)C_6H_3{\cdot}CH{:}CH{\cdot}CO_2H$. Vanillin (225 gr.) was heated with a mixture of acetic

anhydride (675 gr.) and fused sodium acetate (225 gr.) in an oil-bath for 6 hours, when yellow crystals melting at 186–193°, were obtained, which on fractionally recrystallising from alcohol (95%) separated into three fractions: (a) m.p. 190–194°, 70 gr.; (b) m.p. 194–195.5°, 49 gr; and (c) m.p. 223–229°, 10 gr. The last fraction was further recystallised from alcohol and then from glacial acetic acid, from which it separated in faint, yellow crystals melting at 250° (decomp.). (Found: C = 64.21; H = 5.10. Mol. wt., by Rast's method[1], 413.6. $C_{22}H_{20}O_8$ requires C = 64.07; H = 4.86%; Mol. wt. = 412.2).

Hydrolysis. The substance was hydrolysed by means of a 10% aqueous sodium hydroxide on a wire-gauze and on acidification with hydrochloric acid and recrystallisation of the product from dilute alcohol, faint, yellow crystals, m.p. 167.5–168°, were obtained and found to be identical with ferulic acid.

Determination of Groups. The acetyl group was determined by F. Kögl & P. P. Postowsky's method[2] and the methoxyl groups, by the micro-Zeisel method (Pregl, "Die Quantitative Organische Mikroanalyse". p. 178). (Found: CH_3CO = 10.52; 10.23; CH_3O = 14.97; 15.13. $C_{18}H_{11}O_5(OCH_3)_2(CH_3CO)$ requires CH_3CO = 10.44; CH_3O = 15.06%). The numbers of the carboxyl group were determined by conversion into its Ba-salt and subsequent analysis. (Found: CO_2H = 10.98. $C_{21}H_{19}O_6(CO_2H)$ requires CO_2H = 10.91%).

The Methyl Ester. The substance was esterified with diazomethane in ethereal suspension. After evaporating the ether and recrystallising the product from a mixture of ether and benzene, faint, yellow crystals, m.p. 204–205.5°, were obtained. No alternation of melting point was observed on mixing it with a specimen which was obtained synthetically by the method described on p. 21.

Synthesis of Methyl Acetylferuloylferulate. *Acetylferuloyl chloride,* $(CH_3CO_2)(CH_3O)C_6H_3CH:CH\,COCl$. Acetylferulic acid (2 gr.) was treated with thionyl chloride (6 gr.) in a water-bath. After evaporating the excess of thionyl chloride in a vacuum, the raw product was recrystallised from benzene, care being taken to avoid any access of moisture. Faint, brown crystals thus purified melted at 133°–134°.

5.568 mg. gave 3.035 mg. AgCl. (Found: Cl = 13.49. $C_{12}H_{11}O_4Cl$ requires Cl = 13.97%).

Methyl Acetylferuloylferulate, $[(CH_3CO_2)(CH_3O)C_6H_3\cdot CH:CH\cdot CO_2](CH_3O)C_6H_3CH:CH\,CO_2CH_3$. To a solution of 3 gr. of ferulic acid in 15 gr. of pyridine, kept at −15°, the acetylferuloyl chloride obtained from 5 gr. of acetylferulic acid was added and allowed to stand overnight. The product was acidified with dilute sulphuric acid and the precipitate was purified from acetone, glacial acetic acid and then from dilute alcohol. The product

(1) *Ber.*, **55** (1922), 1051.
(2) *Ann.*, **440** (1924), 34.

thus purified was treated with an ethereal solution of diazomethane. After recrystallising from a mixture of ether and benzene, faint, yellow crystals, m.p. 204–205.5°, were obtained.

5,275 mg. gave 12.490 mg. CO_2 and 2.660 mg. H_2O. (Found : C=64.70 ; H=5.64. $C_{21}H_{22}O_8$ requires C=64.57 ; H=5.20%).

Application of the Perkin Reaction to the Derivatives of Vanillin not Containing the Free Phenolic Group. (*a*) *Application to Acetylvanillin.* After heating acetyl vanillin (2 gr.) with fused sodium acetate (1.56 gr.) and acetic anhydride (4.7 gr.) in an oil-bath and recrystallising the product from alcohol, faint, yellow crystals, m.p. 192–193.5°, (m.p. of acetylferulic acid is 195–195.5°), were obtained. However, no acetylferuloylferulic acid could be isolated.

(*b*) *Application to Veratraldehyde.* A mixture of veratraldehyde (10 gr.), fused sodium acetate (12 gr.) and acetic anhydride (27.6 gr.) was heated to boiling for 6 hours. After removing the excess of acetic anhydride, the reaction product was extracted with ether, washed well with water, dried and evaporated. On standing it in a vacuum desiccator, a small quantity of solid was separated from the residual oil and recrystallised from alcohol, from which it separated in colourless crystals, m.p. 181° (yield, 0.5 gr.). 3 : 4-Dimethoxycinnamic acid is stated by Milobedzka to melt at 180–181°.

Application of the Perkin Reaction to p-Hydroxybenzaldehyde. A mixture of p-hydroxybenzaldehyde (15 gr.), acetic anhydride (56 gr.) and fused sodium acetate (18.7 gr.) was heated at 195–200° for 6 hours. After removing the excess of acetic anhydride and boiling twice with water, the residue, m.p. 168–188°, (12 gr.) was separated at first into two parts by using boiling alcohol.

The Part Soluble in Boiling Alcohol. This part was again separated into two portions by using hot water, namely the fraction soluble and insoluble in hot water. On recrystallising each portion from alcohol, colourless crystals (a), m.p. 205.5–206°, were obtained from the former, and faint, yellow crystals (b), m.p. 222–223° (decomp.), from the latter :

4.029 mg. of subst. (a) gave 9.882 mg. CO_2 and 2.026 mg. H_2O ; 0.350 mg. in 3.945 mg. of camphor gave Δt=15.6° (Found : C=64.02 ; H=5.38 ; Mol. wt.=227.5. $C_{11}H_{10}O_4$ requires C=64.07 ; H=4.86% ; Mol. wt.=206.8).

4.022 mg. of subst. (b) gave 10.085 mg. CO_2 and 1.805 mg. H_2O ; 0.105 mg. in 2.070 mg. of camphor gave Δt=5.6° (Found : C=68.19; H=5.00 ; Mol. wt.= 362.3. $C_{22}H_{16}O_6$ requires C=68.16 ; H=4.58% ; Mol. wt.=352.1).

The Part Insoluble in Boiling Alcohol. As this part was insoluble in water or in most organic solvents, it was first freed from impurities by boiling it successively with water, with alcohol and with glacial acetic acid,

(1) *Ber.*, **43** (1910), 2166.

and then recrystallised six times from nitrobenzene, when it separated as a grey, amorphous substance (c), m.p. 231° (decomp.):

4.733 mg. gave 12.139 mg. CO_2 and 2.026 mg. H_2O. (Found: C = 69.94; H = 4.57. $C_{28}H_{22}O_8$ reguires C = 69.89; H = 4.45%).

Hydrolysis. Each of these three substances was hydrolysed with a 15% aqueous sodium hydroxide, when in all these cases only one colourless substance, m.p. 206-207°, was obtained in the almost theoretical yield. G. Eigel[2] gave 206° as the melting point of p-hydroxycinnamic acid.

The Methl Ester of (*b*). Substance (b) was treated with diazomethane in ethereal suspension and the product then purified as in the preparation of methyl acetylferuloylferulate, when faint, yellow crystals, m.p. 166–167°, were obtained and produced no depression of the melting point by admixture with methyl 4-p-acetyloxycinnamoyloxycinnamate which was synthetically obtained by the method described later.

The Methyl Ester of (*c*). The methyl ester, prepared similarly as described above, melted at ca. 200° on being rapidly heated:

4.620 mg. gave 11.860 mg. CO_2 and 2.094 mg. H_2O. (Found: C = 70.01; H = 5.07. $C_{30}H_{24}O_8$ requires C = 70.28; H = 4.73%).

Synthesis of Methyl 4-p-Acetyloxycinnamoyloxycinnamate, $[(CH_3CO_2)C_6H_4{\cdot}CH{:}CH{\cdot}CO_2]\ C_6H_4\ CH{=}CH{\cdot}CO_2CH_3$.

Acetyloxycinnamoyl Chloride, $(CH_3CO_2)\,C_6H_4{\cdot}CH{:}CH{\cdot}COCl$. 4-Acetoxycinnamic acid (0.5 gr.) was converted into its acid chloride, by treating with 2.5 gr. of thionyl chloride similarly as in the preparation of acetylferuloyl chloride, when it separated in colourless crystals, m.p. 118–119°:

7.153 mg. gave 4.446 mg. AgCl. (Found: Cl = 15.37. $C_{11}H_9O_3Cl$ requires Cl = 15.78%).

Methyl 4-p-Acetyloxycinnamoyloxycinnamate. p-Hydroxycinnamic acid (0.062 gr.) was dissolved in a mixture of 0.6 gr. of pyridine and 3 c.c. of absolute ether and kept at −15°. On acidifying with dilute sulphuric acid, faint, yellow precipitate separated, which was recrystallised once from alcohol, and was employed in the preparation of the methyl ester with diazomethane without further purification. The raw product was twice recrystallised from alcohol, when it melted at 166–167°.

4.865 mg. gave 12.273 mg. CO_2 and 2.389 mg. H_2O. (Found: C = 68.79; H = 5.49. $C_{21}H_{18}O_6$ requires C = 68.82; H = 4.95%).

The Application of the Perkin Reaction to 4-Methoxybenzaldehyde. *Synthesis of 4-Methoxycinnamic acid,* $(CH_3O)C_6H_4\,CH{:}CH\,CO_2H$. A mixture of 9 gr. of anisaldehyde, 30 gr. of acetic anhydride and 10 gr. of fused sodium acetate was heated to boiling for six hours. The reaction product thus

(2) *Ber.*, 20 (1887), 2529.

obtained was treated in a similar manner to the purification of veratraldehyde. After removing the excess of acetic anhydride and boiling it with water, 0.6 gr. of faint, yellow crystals, melting at 165° to a milky liquid and becoming clear at 185°, were isolated from the crude product.

In conclusion, the author desires to express his sincere thanks to Professor Hiroshi Nomura for his kind guidance and encouragement.

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ON THE SO-CALLED DIETHYL DICYANOGLUTACONATE AND SOME OF ITS DERIVATIVES.

By **Yoshiyuki URUSHIBARA.**

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The diethyl dicyanoglutaconate was first prepared by G. Errera[1] and by Ruhemann and Browning[2] independently, by the action of ethyl cyanoacetate, sodium ethylate, and chloroform, the sodium derivative being formed intermediately. The formula I was given to the ester and II to the sodium derivative.

$C_2H_5OOC—C(CN)=CH—CH(CN)—COOC_2H_5$ I.
$C_2H_5OOC—C(CN)=CH—CNa(CN)—COOC_2H_5$ II.

Errera's observations are as follows: The diethyl sodio-dicyanoglutaconate is light yellow, glittering needles, has two molecules of water of crystallisation, when it is crystallised from water, and melts at about 265°C. By acidifying a warm aqueous solution of this sodium compound a yellow substance is precipitated, which is recrystallised from benzone and found to be pure diethyl dicyanoglutaconate.

see errata v. 2, p. 936

(Found: C=55.52; H=5.59; H=11.59. $C_{11}H_{12}O_4N_2$ requires C=55.93; H=5.08; N=11.86 %)

The diethyl dicyanoglutaconate melts at 178–179°, is difficultly soluble even in hot benzene, easily soluble in alcohol but *decomposed*. By boiling the spirit solution, the diethyl dicyanoglutaconate is changed into another substance of the formula $C_{11}H_{16}O_6N_2$.

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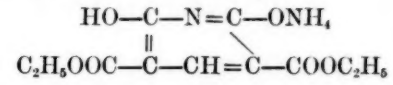
(1) *Ber.*, **31** (1898), 1241.
(2) *J. Chem. Soc.*, **73** (1898), 280.

He thought this substance was the diamide of the dicarboxyglutaconic ester but M. Guthzeit[1] showed that it was the ammonium salt of the diethyl dihydroxydinicotinate of the formula III.



III.

Ruhemann and Browning made similar observations and also obtained some pyridine derivatives. They state as follows:

"Ethylic dicyanoglutaconate dissolves readily in hot acetone, and crystallises from it in yellow, glittering plates which melt and decompose at 187–188°. It was found to contain a small quantity of another substance *which was not removed by repeated recrystallisation.* The following analytical results show that the percentage of carbon in different specimens of the product varies from the theoretical number by one to two percent."

(Found: C=54.07, 54.42, 55.22, 54.65; H=5.55, 5.38, 5.46, 5.42; N=11.50, 11.70 %).

By the action of ethyl cyanoacetate, sodium ethylate and carbon tetrachloride, Otto Dimroth[2] also obtained the same yellow sodium derivative, and from it the free ester melting at 181–183°. He observed that this substance showed a varying melting point according to the mode of heating. His analytical data is N=11.51 %.

G. Errera and F. Perciabosco[3] obtained the same yellow sodium compound by a long boiling of the triethyl sodio-dicyanoaconitate.

A Corrected Idea on the So-called Diethyl Dicyanoglutaconate. This compound was often prepared by the author according to the method of Errera for the purpose of obtaining any brominated derivatives by the action of bromine. The sodium derivative several times recrystallised from hot water was yellow needles, and its properties as well as those of the free ester agreed with the literatures.

After the obtainment of some new derivatives the starting substance, e.i. the diethyl dicyanoglutaconate seemed very doubtful in its chemical composition and constitution.

Preparation of Pure Substance. The diethyl dicyanoglutaconate precipitated from a hot aqueous solution of repeatedly recrystallised sodium derivative, washed with water, and dried, was dissolved in boiling absolute alcohol, filtered while hot and then cooled. The deposited crystals were collected, washed with ether, and dried.

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(1) *Ber.*, **32** (1899), 779.
(2) *Ber.*, **35** (1902), 2881.
(3) *Ber.*, **34** (1901), 3707.

0.2873 gr. of subst. gave 29.2 c.c. of N_2 at 24° and 758 mm. (Found: N = 11.31. $C_{11}H_{12}O_4N_2$ requires N=11.86 %.)

This was again recrystallised from pure acetone, and gave the following analytical result. 0.2616 gr. of subst. gave 26.5 c.c. of N_2 at 22° and 755 mm. (Found: N=11.34 %.)

Once more recrystallised from acetone (that is once from alcohol and twice from acetone). 0.2014 gr. of subst. gave 20.0 c.c. of N_2 at 19.5° and 763 mm. (Found: N=11.38 %).

Each time the taken substance was dried at 100° for half an hour in the stream of dry air, and weighed. After this treatment the yellow colour of the crystals became slightly deeper than before. Errera found in the substance crystallised from alcohol a carbon content too small by one to two percent, which he attributed to decomposition. Thus the determination of nitrogen seemed to lead to the same conclusion.

Another attempt of obtaining a pure substance was made by the replacement of chloroform with iodoform. The author found formerly that the tetraethyl sodio-dicarboxyglutaconate was obtainable in a purer state by using iodoform than by chloroform, and had lighter colour and somewhat higher melting point. In the case of the diethyl dicyanoglutaconate the same result was expected.

The sodium compound formed by using iodoform, after removing the usual red-coloured by-product by repeated recrystallisation from hot water, became nearly *colourless* crystals, melting at about 265°. On heating over 100° it turned yellow. With chloroform a *yellow* substance was always obtained, and thus it was ascertained that the colour was not essential, but caused by impurities. Between the melting point of the two kinds of preparations no remarkable difference was observed.

This colourless sodium compound was converted into the free ester by the ordinary procedure. The yellow crystals precipitated by hydrochloric acid were washed with water, dried, and recrystallised from pure acetone. This purified substance melted at 183° (corr.) and gave the following analytical result.

0.1495 gr. of substance dried at 100° gave 14.9 c.c. of N_2 at 20° and 766 mm. (Found: N=11.43 %.)

This corresponds to the formula $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2}H_2O$, which requires N=11.43 %.

Composition of the So-called Diethyl Dicyanoglutaconate. The following facts suggest a great doubtfulness in the nature of this compound. (I) Its yellow colour, whilst the sodium derivative was ascertained to be colourless. cf. The tetraethyl dicarboxyglutaconate, which is colourless liquid and its sodium derivative is light yellow crystals. (2) Its high melting point,

whilst the tetraethyl dicarboxyglutaconate and the triethyl α-cyano-γ-carboxyglutaconate are both liquid at the ordinary temperature. (3) When an aqueous solution of the sodium compound is acidified, the free ester separates out only after a while, not immediately. (4) Its small solubilities in various solvents. It is practically insoluble in benzene and ether, and only slightly soluble in cold alcohol and cold acetone. (5) The low value of nitrogen content. In both Errera's and Ruhemann's analytical data, the sodium derivative shows satisfactory numbers, while the free ester, obtainable by a simple treatment from the former, varies from the theoretical number by an impermissible amount.

The purest specimen obtained by using iodoform and recrystallised from acetone, contained 11.43 % of nitrogen as mentioned above, which corresponded to the formula $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2} H_2O$. The contents of carbon and hydrogen were determined.

0.1959 gr. of substance dried at 100° gave 0.3868 gr. CO_2 and 0.0928 gr. H_2O. (Found: C = 53.87; H = 5.30. $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2} H_2O$ requires C = 53.88; H = 5.31 %.)

There can be no hesitation in giving the formula $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2} H_2O$ to the diethyl dicyanoglutaconate.

Errera and Ruhemann got probably only impure substances and calculated by an incorrect formula. One of Ruhemann's specimens, that showed the smallest contents of carbon (54.07 %) and nitrogen (11.50 %), although there is no knowing if the substances for both determinations belonged to the same specimen or not, may really be the purest, which he might considered as the least pure. Errera observed that the crystals from alcohol contained too small carbon, but did not noticed the presence of half a molecule of water. Ruhemann obtained an ammonia derivative of the formula $C_{11}H_{12}O_4N_2 \cdot NH_3 \cdot \frac{1}{2} H_2O$, but did not detect half a molecule of water contained in the original ester.

Constitution of the Diethyl Dicyanoglutaconate. The triethyl dicyanoaconitate [145–146°], $C_2H_5OOC-C(CN)=C(COOC_2H_5)-CH(CN)-COOC_2H_5 + \frac{1}{2} H_2O$[1], and the methenylbismalonitrile imidether [244°], $(CN)_2C=CH-CH(CN)-C(NH)-OC_2H_5 + \frac{1}{2} H_2O$[2], obtained from the corresponding sodium derivatives by acidifying their aqueous solutions have also half a molecule of water. In both cases it was not determined whether the half molecule of water was the water of crystallisation or combined constitutionally. The present author made no close investigation of these two substances, but if such derivatives of the dinitrile of the glutaconic acid usually have half a

(1) G. Errera und F. Perciabosco, *Ber.*, **34** (1901), 3704.
(2) W. Zoernig, *J. prakt. Chem.*, **74** (1906), 435.

molecule of water when they are formed from the sodium derivatives by acidifying their aqueous solutions, it will not, probably, be a water of crystallisation.

Dehydration of the Ester. A substance dried in the desiccator at the ordinary temperature showed practically no decrease in weight on heating half an hour at 100° in the stream of dry air. 0.3114 gr. of the substance dried at 100° weighed 0.3108 gr. after one hour heating at about 130°, and 0.3104 gr. after more one hour heating at 150°, in the stream of dry air. The water in the diethyl dicyanoglutaconate was unremovable even by heating at 150°

Molecular Weight. Although the ester is not sufficiently soluble in boiling acetone, and the elevation of the boiling point is small, an ebullioscopic determination in this solvent was tried. The number 406 was obtained as the molecular weight, and it seemed that the diethyl dicyanoglutaconate had the molecular formula $(C_{11}H_{12}O_4N_2)_2H_2O$.

Chemical Properties. The sodium derivative of the diethyl dicyanoglutaconate does not evolve ammonia on heating with caustic alkali, but when the free ester is heated with caustic alkali, the ammoniacal odour is evidently perceived. Some of the nitrogen atoms in the free ester are more easily detached by alkali than those in the sodium compound. This indicates an undeniable difference in the constitution of these two compounds.

All these facts and the investigation of the bromine addition compound, which will be described later, show that the constitution of the diethyl dicyanoglutaconate will probably be represented by one of the following formulæ.

$$(C_{10}H_{12}O_4N)—C(NH)—O—C(NH)—(C_{10}H_{12}O_4N) \qquad \text{IV.}$$
$$(C_{10}H_{12}O_4N)—CO—NH—C(NH)—(C_{10}H_{12}O_4N) \qquad \text{V.}$$

J. F. Thorpe[1] indicated that a nitrile of the formula VI would pass into an imino piperidine of the formula VII.

$$CH_2\begin{cases}CH_2\cdot CONH_2\\CH_2\cdot CN\end{cases} \qquad \text{VI.} \qquad\qquad CH_2\begin{cases}CH_2\cdot CO\\CH_2\cdot C(NH)\end{cases}NH \qquad \text{VII.}$$

In the present case the formula V is also more probable than IV, for it can be supposed that this compound would be formed by the condensation of a monoamide-mononitrile and a dinitrile.

This assumption is not contradictory to the fact that some pyridine derivatives were obtained from the ester, for a compound with such a constitution will easily be split into two similar molecules.

(1) *J. Chem. Soc.*, **99** (1911), 422. Further cf. *J. Chem. Soc.*, **99** (1911), 1684; **115** (1919), 686; **117** (1920), 1465.

It is supposed that an analogous discussion may be made on the triethyl dicyanoaconitate and the methenylbismalonitrile imidether.

Action of Bromine on the Diethyl Dicyanoglutaconate. The diethyl dicyanoglutaconate was introduced in pure chloroform (about ten times in weight), and bromine (dehydrated by shaking with concentrated sulphuric acid) was added drop by drop. By the time when the quantity of bromine reached to four atoms to one molecule of the ester (refered to the formula $(C_{11}H_{12}O_4N_2)_2\,H_2O$), the solid entered completely into solution, and during the addition of further four atoms of bromine, brick-red crystals were separating out. (In the dark the appearance of the crystals was somewhat delayed.) When the increase in amount of the crystals ceased, they were collected, washed with pure benzene (dehydrated on sodium) and dried in vacuum. When the brominated product was left in its mother liquor for a long time, it was accompanied by another substance, which also crystallised from the filtrate of the former and was considered to be the product of a secondary change.

This experiment was often repeated, and specimens of various purities were obtained. This substance melts at 146–149°, has a large proportion of free bromine, and is so unstable that it is decomposed in ether, alcohol, and water, but crystallises unchanged from a hot pure benzene solution on cooling. As shown in the following pages, this substance is transformed into the diamide hydrobromide, $C_{11}H_{16}O_6N_2{\cdot}HBr$ and then into the picrate, $C_{11}H_{16}O_6N_2{\cdot}C_6H_2\,(NO_2)_3OH$, which indicates that it is merely a molecular addition compound.

0.2247, 0.2028, 0.2960, 0.2750, 0.1199 gr. subst. (each belonging to a different specimen), gave 0.2809, 0.2483, 0.3730, 0.3457, 0.1520 gr. AgBr respectively. 0.1701, 0.6071, 0.4638 gr. subst. gave 19.8 (26.5°, 760 mm.), 29.4 (29°, 758 mm.), 24.4 c.c. (31°, 751 mm.) nitrogen respectively. (Found: Br=53.6, 52.10, 53.63, 53.50, 53.95; N=5.27, 5.24, 5.57 %).

Determination of Free Bromine. The iodometry was not successful in this case, for the liberation of iodine was incomplete. The method of analysis was as follows. The substance was weighed in a watch glass and placed in a beaker. A freshly prepared aqueous solution of sulphur dioxide, which should be free from sulphuric acid, was poured in the beaker and heated on the water bath. The crystals were dissolved to a colourless solution. Most of the excess of sulphur dioxide was then expelled by adding hydrochloric acid and heating. The formed sulphuric acid was determined as barium sulphate by the ordinary method. From the mother liquor of the barium sulphate a white substance crystallised out, which was identified with the diethyl dihydroxydinicotinate by its melting point (about 200°), and its reddish coloration on adding ferric chloride, the experimental fact

described on p. 34 and 35 being taken into consideration. One molecule of barium sulphate corresponds to two atoms of bromine.

0.5004, 0.2887, 0.3617 gr. subst. gave 0.3287, 0.1910, 0.2397 gr. $BaSO_4$ respectively. (Found: Free Br=45.0, 45.3, 45.4. $(C_{11}H_{12}O_4N_2)_2H_2O.HBr.Br_6$ requires, total Br=53.3; free Br=45.7; N=5.33 %).

H. L. Wheeler and D. T. Walden[1] obtained many addition compounds of the general formula $(C_6H_5NHCOCH_3$ or derivative$)_2.HX.X_n$, where X represents Br or I, for instance, $(m\text{-}NO_2C_6H_4NHCOCH_3)_2HBr.Br_6$. At first they obtained some compounds of this series by the action of bromine on the meta-nitroacetanilide in chloroform. If the bromine was free from hydrogen bromide and the solvent was not attacked by bromine, no addition took place. Thus in carbon bisulphide they could not get the addition compounds. The present author also ascertained that the diethyl dicyanoglutaconate gave no addition compound in carbon bisulphide. But a long standing caused a substitution in a part of the substance and some brominated product separated out. The formula with two imino-groups given to the diethyl dicyanoglutaconate seems to be quite correct.

The Diamide Hydrobromide. When the bromine addition compound was introduced in commercial ether it changed into a white crystalline compound. This transformation was neither realised in absolute ether, nor in the presence of an excess of bromine, but promoted by light. Hence this reaction proceeded by liberating bromine and combining with water, and required more hydrogen bromide than the bromine addition compound originally contained. The ether in which the new substance was formed, was brown with bromine and left nearly no residue on evaporation. For the purpose of preparation it is better to use a sufficient amount of ether saturated with water. After the disappearance of the original brown crystals, the product is collected, washed with ether and dried. (The yield is theoretical, see under).

0.1369, 0.2952, 0.2206, 0.1460 gr. subst. gave 0.0733, 0.1587, 0.1173, 0.0785 gr. AgBr respectively. 0.1982, 0.2856 gr. subst. gave 14.3 (30°, 750 mm.), 20.7 c.c. (29°, 756 mm.) nitrogen respectively. (Found: Br=22.79, 22.88, 22.63, 22.88; N=7.73, 7.83. $C_{11}H_{12}O_4N_2.2H_2O.HBr$ requires Br=22.79; N=7.96 %).

This compound forms light, silky, white needles, does not show a sharp melting point, but decomposes to a dark red liquid when heated near 180°. It is soluble in water and alcohol, much more when heated, but insoluble in ether. The alcoholic solution is slightly fluorescent, and gives no coloration on adding ferric chloride. From a hot concentrated solution in water or

(1) *Am. Chem. J.*, 18 (1896), 86.

alcohol the unchanged substance crystallises out on cooling. It dissolves also in hot concentrated hydrobromic acid (ca. 40 %) and crystallises from it unchanged. This substance does not liberate ammonia when boiled with caustic alkali, and only a long boiling with strong alkali decomposes it into ammonia and other substances. The aqueous solution is acidic and precipitates silver bromide on adding silver nitrate.

In every point it does not resemble[1] with the ammonium salt of the diethyl dihydroxydinicotinate, which was formed by adding two molecules of water to the diethyl dicyanoglutaconate in spirit solution but possesses a great likeliness for being a hydrobromide of an acid amide. Many acid amides give molecular compounds of the formula $2R.CONH_2.HX$ with hydrogen halide. Comparison of their properties with those of the present substance indicates that it belongs to the compound of this type, and it has two amide-groups in one molecule. The hydrohalides of amides are easily formed from nitriles in various reactions, where necessary water, or such substances as to give water by reaction, and hydrogen halide are present.[2]

The diethyl dicyanoglutaconate gave directly a slightly yellowish compound containing bromine and 7.86% of nitrogen, by the action of ether shaken with concentrated hydrobromic acid.

Moreover the hydrobromide gives the picrate of the formula $C_{11}H_{16}O_6N_2.C_6H_2(NO_2)_3OH$ which will be described in details in the following paragraphs.

Picrate of the Diamide. When the diamide hydrobromide was mixed with the picric acid both in alcoholic solutions, yellow, glittering needles separated out, which were collected, washed with alcohol several times and dried in the air-bath. This picrate melted at 196–197° (corr.) and contained no bromine, whilst the mother liquor showed the reaction of the bromine ions.

0.2214, 0.2189 gr. subst. gave 28.0 (26°, 754 mm.), 27.8 c.c. (25.5°, 755 mm.) nitrogen respectively. (Found: N=13.85, 13.97. $C_{11}H_{16}O_6N_2.C_6H_2(NO_2)_3OH$ requires N=13.97%).

The value of carbon and hydrogen did not exactly agree with the formula, but was sufficient to exclude such a formula as $(C_{11}H_{12}O_4N_2)_2C_6H_2(NO_2)_3OH$, which requires N=14%.[3]

	Found	$C_{11}H_{16}O_6N_2.C_6H_2(NO_2)_3OH$	$(C_{11}H_{12}O_4N_2)_2.C_6H_2(NO_2)_3OH$
C	41.9%	40.7%	46.8%
H	3.5%	3.8%	3.9%

0.2146 gr. of the picrate weighed 0.2141 gr. after heating at 150° for half

(1) See page 35.

(2) Colson, *Bull. soc. chim.*, [3] **17** (1897), 57. A. Pinner und Fr. Klein, *Ber.*, **10** (1877), 1896. F. Henle und G. Shupp, *Ber.*, **38** (1905), 1370.

(3) Nitro-compounds often give deviated results in analysis, unless a special care is taken.

an hour in the stream of dry air. Therefore the two molecules of water which came from the hydrobromide were not a water of crystallisation but combined constitutionally. The picrate agreed in appearance very closely with the picrates of the acetamide and formamide. The picric acid almost always gives the binary molecular compounds, when it enters into so-called picrates, whatever the constitution of the other substances may be. In this case the diamide also produced a binary compound, like the acetamide. The picrate is difficultly soluble in absolute alcohol, but easily soluble in hot spirit. It is not decomposed by, and when the two components are present also formed in, a moderately strong hydrobromic acid.

The same picrate was formed when the diethyl dicyanoglutaconate was mixed with the picric acid in alcohol containing some water. When the solutions of the diethyl dicyanoglutaconate and of the picric acid both in absolute alcohol were mixed, a brown clear solution resulted. On adding a few drops of water to this solution the picrate separated out in fine crystals immediately, whilst this picrate is more soluble in alcohol containing water than in absolute alcohol. Without the addition of water the picrate crystallised slowly taking water from surroundings.

0.1034 gr. of substance gave 13.0 c.c. of N_2 at 24.5° and 758 mm. (Found: N = 13.95%.) Melting point: 196.5°. The substance mixed with the picrate from the hydrobromide melted at 195.5°.

Finally the same picrate was formed when the bromine addition compound of the diethyl dicyanoglutaconate was mixed with the picric acid in alcoholic solution. Melting point: 195.5°. The substance mixed with the picrate from the hydrobromide melted at 196°.

The three compounds, diethyl dicyanoglutaconate, its bromine addition compound, and the diamide hydrobromide gave the same picrate.

Transformation of the Diamide Hydrobromide into the Diethyl Dihydroxydinicotinate. The diamide hydrobromide was boiled with dilute hydrobromic acid. It entered into solution at first, and in the course of a few minutes a solid separated, which rapidly increased in quantity. When cold this was collected. The mother liquor gave ammonia on heating with alkali. This substance was treated with cold concentrated hydrochloric acid. After adding water the solid was collected, washed and dried.

For comparison, the diethyl dihydroxydinicotinate was prepared by Ruhemann's method.[1] The substance obtained by the hydrolysis of the diethyl dicyanoglutaconate with dilute hydrobromic acid was not already the ammonium salt but the free diethyl dihydroxydinicotinate, for it gave no ammonia on heating with alkali, and the mother liquor gave it. But to

(1) *J. Chem. Soc.*, 73 (1898), 284.

complete the reaction the solid was treated with cold concentrated hydrochloric acid, as described by Ruhemann. The substance obtained from the hydrobromide was compared with that from the diethyl dicyanoglutaconate, and found to be identical. The former, as well as the latter, was readily soluble in chloroform, gave the red coloration on adding ferric chloride, and melted at the same point (199° not corr.) The three compounds, the diethyl dicyanoglutaconate, its bromine addition compound, and the diamide hydrobromide, are all changeable into the diethyl dihydroxydinicotinate.

The ammonium salt of the diethyl dihydroxydinicotinate was prepared according to Errera's method[1] by the hydrolysis of the diethyl dicyanoglutaconate in spirit. On boiling, the solution of the diethyl dicyanoglutaconate in spirit became gradually colourless and a solid separated out, the mother liquor remaining colourless, whilst Errera observed that the mother liquor became intensively yellow, which was probably due to impurities.

This ammonium salt gave no product with picric acid in alcohol. By heating with caustic alkali it liberated ammonia. By a dilute acid it was changed into the free ester, for by Ruhemann's method the ammonium salt was not obtained. On adding a ferric chloride solution to the substance suspended (not dissolved) in alcohol, at first no coloration, and then gradually reddish violet coloration occurred, which shows that the ammonium salt was transformed into the free ester by the ferric chloride solution.

The compound $C_{11}H_{16}O_6N_2$, which was obtained as its hydrobromide $C_{11}H_{16}O_6N_2 \cdot HBr$ and picrate $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$, differs from the ammonium salt of the diethyl dihydroxydinicotinate with the same composition and obtainable from the same mother substance, and is changeable into the diethyl dihydroxydinicotinate. Hence it can be no other compound than the diamide of the dicarboxyglutaconic ester, which corresponds to the formula $NH_2CO–C(COOC_2H_5)=CH–CH(COOC_2H_5)–CONH_2$ and should be called the "diethyl $\alpha\gamma$-dicarbamylglutaconate." No amide of this type has ever been obtained, and in cases where such amides should be formed, a ring formation or splitting into a propene chain took place.[2]

In those reactions producing the bromine addition compound of the diethyl dicyanoglutaconate, the diamide hydrobromide, and the picrate, no heat was applied. All the transformations proceeded at the ordinary temperature. Hence it is natural to suppose that there took place no extraor-

(1) *Ber.*, **31** (1898), 1241.

(2) See page 27 and Errera, *Ber.*, **33** (1900), 2973; Ruhemann and Morrell, *J. Chem. Soc.*, **59** (1891), 743; ibid., **61** (1892), 791; ibid., **63** (1893), 874; Guthzeit und Laska, *J. prakt. Chem.*, **58** (1898), 419; Guthzeit und Haussmann, *Ann.*, **285** (1895), 61 u. 97. Further cf., J. F. Thorpe and his collaborators, *J. Chem. Soc.*, **85-117** (1904-1920), "The Formation and Reactions of Imino Compounds. Part I-Part XX".

dinary change as the ring formation. The free diamide has not yet been isolated.

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Summary.

1. The so-called diethyl dicyanoglutaconate has the composition $(C_{11}H_{12}O_4N_2)_2H_2O$ and the constitution is considered to be represented by the formula $(C_{10}H_{12}O_4N)$–CO–NH–C(NH)–$(C_{10}H_{12}O_4N)$.

2. The diethyl sodiodicyanoglutaconate is colourless when pure.

3. By the action of bromine on the so-called diethyl dicyanoglutaconate an addition product is obtained, which has the composition $(C_{11}H_{12}O_4N_2)_2 \cdot H_2O \cdot HBr \cdot Br_6$. This is changed into the diamide hydrobromide, $C_{11}H_{16}O_6N_2 \cdot HBr$, in ether containing water.

4. The picrate of the diamide, $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$, is obtained from the diamide hydrobromide, from the bromine addition compound, and from the so-called diethyl dicyanoglutaconate. These three compounds are all changeable into the diethyl dihydroxydinicotinate.

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